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(54) **Title:** METHOD FOR PREPARING ROD-SHAPED POLYANILINE NANOPARTICLES HAVING HIGH CONDUCTIVITY USING MICRO-EMUSION POLY-MERIZATION

(57) **Abstract:** A method for preparing polyaniline nanoparticles having rod shapes and high conductivity using microemulsion polymerization is disclosed. The method for preparing polyaniline nanoparticles includes the steps of adding a surfactant into a mixed solvent including water and an organic solvent, and stirring the surfactant to form a micelle, preferably at the temperature of - 30 to 0 ° C; adding aniline monomer into a reaction solution containing the micelle, and polymerizing the aniline monomer with a dopant and an oxidizing agent to form polyaniline; and adding excess organic solvent to the reaction solution to separate the polyaniline and the micelle.

Description

METHOD FOR PREPARING ROD-SHAPED POLYANILINE NANOPARTICLES HAVING HIGH CONDUCTIVITY USING MICRO-EMUSION POLYMERIZATION

Technical Field

[1] The present invention relates to a method for preparing polyaniline nanoparticles, and more particularly, to a method for preparing polyaniline nanoparticles having rod shapes and high conductivity using low-temperature micro-emulsion polymerization.

Background Art

[2] With the rapid development of electronic and information technology, the application areas of a conductive material have been diversified, and researches on a conductive polymer which is capable of replacing a conductive metallic material have been actively carried out. The conductive polymer can be utilized in various areas, such as an electromagnetic shielding, an alternative material of Indium tin oxide(ITO), an alternative material of carbon fiber, a magnetic recording medium, an optical storage, a light emitting device(LED), a cathode material of lithium ion battery, a light transmission material, and so on.

[3] When the conductive polymer is produced in the form of nanoparticles, the polymer has more desirable physical properties due to the small sizes of the nanoparticles than a conductive polymer of a bulk form. The nanoparticle is a material having the size of between a molecule and a bulk solid, and generally has the size of 1 to 100 nanometers. The nanoparticle has different magnetic, optical and electrical properties from a molecule and/or a bulk solid, and the specific properties of the nanoparticle are sometimes called as 'Quantum size effect'. Thus, the nanoparticle is also sometimes called as 'Quantum dot'.

[4] Polyaniline, one of the representative conductive polymers, is a black colored polymer which is produced by oxidation-polymerization of aniline monomer in acidic solution, and conventionally called as 'aniline black'. In the middle of nineteen eighties, it is discovered that the conductivity of polyaniline dramatically increases when protonic acid is doped into the polyaniline. After that discovery, polyaniline have attracted much attention in the art as a desirable conductive polymer. Meanwhile, polyaniline and its derivatives have further advantages in that they are easy to produce,

inexpensive, and have desirable atmospheric and thermal stabilities. When an electromagnetic shielding is produced by dispersing polyaniline into other non-conductive polymer matrix, polyaniline should be uniformly dispersed into the matrix, and the two materials should form a uniform complex without inducing phase separations between the two polymers. If polyaniline in the form of nanoparticles is used for this purpose, polyaniline is more uniformly dispersed in the matrix than polyaniline of micro-size particles, and more uniform polyaniline filler/matrix complex can be formed. In addition, as the conductivity of polyaniline filler increases, the conductivity of the complex increases, and more desirable electromagnetic shielding can be obtained. Therefore, there is an increasing need in the art for polyaniline of high conductivity and nanoparticle size.

Disclosure of Invention

Technical Problem

[5] Therefore, it is an object of the present invention to provide a method for preparing polyaniline nanoparticles having rod shapes and high conductivity.

[6] It is other object of the present invention to provide a method for preparing polyaniline nanoparticles which is capable of reducing the amount of the necessary surfactant in a microemulsion polymerization.

[7] It is another object of the present invention to provide a method for preparing polyaniline nanoparticles which is capable of reducing the amount of the necessary reactants and includes simple reaction steps.

[8] It is another object of the present invention to provide a method for preparing polyaniline nanoparticles which are useful as electrical and magnetic materials, such as electromagnetic shielding, a chemical sensor, a magnetic recording medium, and so on.

Technical Solution

[9] In order to achieve these and other objects, the present invention provides a method for preparing polyaniline nanoparticles by using microemulsion polymerization, which comprises the steps of adding a surfactant into a mixed solvent including water and an organic solvent, and stirring the surfactant to form a micelle; adding aniline monomer into a reaction solution containing the micelle, and polymerizing the aniline monomer with a dopant and an oxidizing agent to form polyaniline; and adding excess organic solvent to the reaction solution to separate the polyaniline and the micelle. Preferably, the micelle formation step is carried out at the temperature of -30 to 0 ° C, the organic solvent in the mixed solvent can be selected from the group consisting of methanol,

ethanol, butanol, octanol, decanol and the mixtures thereof, and the amount of the organic solvent is 20 to 40 weight% in the mixed solvent.

Mode for Invention

[10] A more complete appreciation of the invention, and many of the attendant advantages thereof, will be better appreciated by reference to the following detailed description.

[11] The method for preparing polyaniline nanoparticles according to the present invention produces polyaniline by carrying out a microemulsion polymerization at very low temperature, and thereby reduces the amount of the surfactant required in the microemulsion polymerization, and improves the conductivity and the yield of the produced polyaniline.

[12] In order to produce the polyaniline nanoparticles according to the present invention, micelles should be formed by adding a surfactant into a reaction solvent at the temperature of less than 0 ° C, preferably at the temperature of -30 to -10 ° C, and more preferably at the temperature of about -20 ° C, and stirring the surfactant for 20 to 40 minutes, and preferably for about 30 minutes. In the present invention, the micelle formation step is carried out at the very low temperature. Therefore, in order to prevent the freezing of the solvent, a mixed solvent including water and an organic solvent is used for the micelle formation step. The preferable organic solvent includes methanol, ethanol, butanol, octanol, decanol or the mixtures thereof, and the preferable water is distilled water. The ratio of the organic solvent and water can be varied under the condition that the freezing of the solvent is prevented at the reaction temperature. The preferable and exemplary amount of the organic solvent is 20 to 40 weight% in the mixed solvent, and more preferably about 30 weight%. When the amount of the organic solvent is less than 20 weight%, the temperature of the micelle formation step cannot be sufficiently lowered. When the amount of the organic solvent is more than 40 weight%, the micelles formation may not be sufficiently carried out. In addition, when the temperature of the micelle formation step is less than -30 ° C, the micelles formation may not be sufficiently carried out. When the temperature of the micelle formation step is more than 0 ° C, the amount of the necessary surfactant cannot be reduced sufficiently.

[13] The surfactant, which is added to the mixed solvent, can be a cationic surfactant, an anionic surfactant, or the mixtures thereof. The preferable examples of the cationic surfactant include octyltrimethylammonium bromide (OTAB), decyltrimethylammonium bromide (DeTAB), dodecyltrimethylammonium bromide (DTAB), and

the mixtures thereof. The preferable examples of the anionic surfactant include sodium dodecylsulfate(SDS), sodium dioctylsulfosuccinate and the mixtures thereof. The preferable amount of the surfactant is 0.8 to 2.5 weight part for 100 weight part of the mixed solvent. When the amount of the surfactant is less than 0.8 weight part, the micelle may not be properly formed. When the amount of the surfactant is more than 2.5 weight part, the micelle may be transformed into undesirable shapes from the rod shape. The amount of the surfactant used in the present invention is about 1/10 compared to the amount of the surfactant used in a microemulsion polymerization at room temperature. This might be due to the fact that (i) CMC decreases at low temperature, and thereby, the concentration of the surfactant can be greater than CMC 2 even when a small amount of the surfactant is used, and (ii) the organic solvent, which is included in the mixed solvent for preventing the solvent from being freezing, works as a cosurfactant. The term 'CMC' represents 'Critical Micelle Concentration' which is a concentration capable of forming micelle by surfactant association, and the shape of the micelle varies according to the type and concentration of the surfactant. Generally, when the concentration of the surfactant is more than CMC1, sphere shaped micelles are formed, and when the concentration of the surfactant is more than CMC2, rod shaped or hexagonal shaped micelles are formed. Meanwhile, when the concentration of the surfactant is between the CMC1 and CMC2, the produced micelles are transparent in the solution and invisible by a naked eye. When the concentration of the surfactant is more than CMC2, the produced micelles are invisible by the naked eye and the solution becomes opaque. Namely, the shapes of the micelles are difficult to determine by the naked eye. Therefore, the shape of the polymer polymerized in the micelles is observed with apparatus, such as TEM(Transmission Electron Microscope), SEM(Scanning Electron Microscope) and so on, to determine the concentration of the surfactant. In case that the CMC 1 and CMC 2 of a surfactant at room temperature are known, the CMC 1 and CMC 2 can be referenced for the purpose of the present invention.

[14] After forming micelles with the surfactant, stirring of the reaction solution is carried out while adding aniline monomer as the monomer of the conductive polymer. In addition, a dopant and an oxidizing agent are added thereto to initiate the polymerization reaction. The preferable amount of the aniline monomer is about 0.75 to 2.5 weight part for 100 weight part of the mixed solution containing micelles. When the amount of the aniline monomer is less than 0.75 weight part, all of the micelle may not be used as a nano-reactor. When the amount of the aniline monomer is more than 2.5

weight part, the micelles may not receive all of the aniline monomer, and the deformation of micelles may occur.

[15] The dopant is used to increase the conductivity of the polymerized polyaniline, and to adjust the acidic condition of the reaction solution for rapid and stable reaction. Exemplary dopant includes protonic acid such as hydrochloric acid, sulfuric acid, phosphoric acid, the mixtures thereof, and so on. For increasing the conductivity of the produced polymer, sulfuric acid is more preferable than hydrochloric acid as the dopant. The preferable amount of the dopant is 1 to 3 moles for 1 mole of the aniline monomer. When the amount of the dopant is less than 1 mole, the conductivity of the produced polymer may not be satisfactory. When the amount of the dopant is more than 3 moles, the conductivity of the produced polymer does not additionally increase, but the phase of the polymer may be deformed.

[16] The oxidizing agent is used to polymerize the aniline monomer, and the examples of the oxidizing agent includes ammonium persulfate ($(NH_4)_2S_2O_8$), potassium peroxodisulfate ($K_2O_8S_2$), and so on. The preferable amount of the oxidizing agent is 0.2 to 0.8 mole for 1 mole of the aniline monomer, and the more preferable amount is about 0.5 mole for 1 mole of the aniline monomer. When the amount of the oxidizing agent is less than 0.2 mole, the polymerization of the aniline monomer may not be satisfactory. Even when the amount of the oxidizing agent is more than 0.8 mole, the polymerization speed of the aniline monomer and the polymerization efficiency may not further increase. The oxidizing agent can be added to the reaction solution containing the aniline monomer and the dopant. Alternatively, the oxidizing agent can be dissolved with a dopant, such as hydrochloric acid, sulfuric acid, and so on, and the mixture of the oxidizing agent and the dopant can be added to the reaction solution containing the aniline monomer. More preferably, the oxidizing agent and the dopant are added to the reaction solution after stirring the solution containing micelles and the aniline monomer for about 30 minutes. During the stirring, the aniline monomers are fully incorporated into the interior of the micelles. The reaction time of the polymerization reaction is about 8 to 16 hours, and preferably about 12 hours, and the reaction temperature is preferably maintained to be same with the reaction initiation temperature.

[17] After completing the aniline polymerization, the surfactant is removed to separate the polyaniline nanoparticles produced in the micelles. In order to remove the surfactant and reaction by-products, the reaction solution is poured into a separatory funnel, and excess organic solvent such as methanol, acetone, the mixtures thereof, and

so on, is added thereto. Then the surfactant and the reaction by-products dissolve and are moved into the organic layer. By discarding the upper organic layer, an aqueous solution containing precipitated polyaniline nanoparticles is obtained. Then, by evaporating the aqueous solution at room temperature, the target polyaniline nanoparticles can be obtained.

[18] From the TEM(Transmission Electron Microscopy) analysis of the obtained polyaniline nanoparticles, it is confirmed that rod shaped nanoparticle having the width of about 20 nanometers and the length of about several hundreds nanometer is produced. When the temperature is lowered, the rod shaped nanoparticles are produced even though the more amount of the surfactant is used. The conductivity of the produced nanoparticle is about 50 to 200 S/cm, which is higher than the conductivity of the nanoparticles produced at room temperature. It is also discovered in the present invention that, at low temperature, anionic surfactant is more preferable than the cationic surfactant for increasing the conductivity of the polyaniline nanoparticles. In addition, sulfuric acid is more preferable as the dopant for increasing the conductivity of the polyaniline nanoparticles. Therefore, according to the present invention, rod shaped polyaniline nanoparticles having a high conductivity can be effectively produced with a small amount of the surfactant.

[19] Hereinafter, the preferable examples of the present invention are provided for better understanding of the present invention. However, the following examples are to illustrate the present invention, and the present invention is not limited by the following examples.

[20] [Example 1] Manufacture of polyaniline nanoparticles using cationic surfactant and hydrochloric acid dopant at the reaction temperature of -20 ° C

[21] The reaction temperature was maintained to -20 ° C with a temperature controlling bath, and a mixed solvent including 40 mℓ of distilled water and 20 mℓ of ethanol was used as a reaction medium. 0.5g of decyltrimethylammonium bromide was added to the mixed solvent, and stirred for about 20 minutes to form micelles. Then, 1g of aniline monomer was dropwisely added to the reaction solution by a pipette. The added aniline monomer further stirred for 30 minutes to fully insert the aniline monomer into the interior of the micelles. Meanwhile, 1.125g of ammonium persulfate(oxidizing agent) was dissolved with 6 mℓ of 4M sulfuric acid (mole ratio of aniline/ ammonium persulfate = 1/0.5), and the mixture was added to the reaction solution. While maintaining the reaction temperature to -20 ° C, the reaction solution was stirred for 12 hours to polymerize the aniline monomer. After completing the

polymerization reaction, the reaction solution was poured into a separatory funnel, and excess methanol was added thereto to dissolve the surfactant and reaction by-products. To obtain the precipitated polyaniline nanoparticles, the upper layer of the reaction solution, i.e., the methanol layer was removed by using a pipette, and the remaining layer containing nanoparticles was evaporated at room temperature. The formation of the polyaniline nanoparticles was confirmed with FT-IR analysis. From the TEM(Transmission Electron Microscopy) analysis of the obtained polyaniline nanoparticles, it is confirmed that the rod shaped nanoparticle having the width of about 20 nanometers and the length of about several hundreds nanometer is produced. The conductivity of the obtained nanoparticle was 50 to 80 S/cm.

[22] [Example 2] Manufacture of polyaniline nanoparticles using cationic surfactant and sulfuric acid dopant at the reaction temperature of -20 ° C

[23] Except for using 0.5g of octyltrimethylammonium bromide as the surfactant, and using 10 mℓ of 2M sulfuric acid as the dopant instead of 6 mℓ of 4M hydrochloric acid, polyaniline nanoparticles were produced according to the method described in Example 1. The formation of the polyaniline nanoparticles was confirmed with FT-IR analysis. From the TEM(Transmission Electron Microscopy) analysis of the obtained polyaniline nanoparticles, it is confirmed that the rod shaped nanoparticle having the width of several tens nanometers and the length of about several hundreds nanometer is produced.

[24] [Example 3] Manufacture of polyaniline nanoparticles using anionic surfactant and sulfuric acid dopant at the reaction temperature of -20 ° C

[25] Except for using 0.3g of sodium dodecylsulfate as the surfactant, and using 10 mℓ of 2M sulfuric acid as the dopant instead of 6 mℓ of 4M hydrochloric acid, polyaniline nanoparticles were produced according to the method described in Example 1. The formation of the polyaniline nanoparticles was confirmed with FT-IR analysis. From the TEM(Transmission Electron Microscopy) analysis of the obtained polyaniline nanoparticles, it is confirmed that the rod shaped nanoparticle having the width of several tens nanometers and the length of about several hundreds nanometer is produced. The conductivity of the obtained nanoparticle was 150 to 200 S/cm, which is much higher than the conductivity of polyaniline nanoparticles produced with a cationic surfactant.

[26] As described above, the method for preparing polyaniline nanoparticles according to the present invention performs the microemulsion polymerization at very low temperature of about -20 ° C. Therefore, the amount of the surfactant required for the

microemulsion polymerization is reduced to about 1/10 compared to the amount of the surfactant used in a microemulsion polymerization at room temperature, which reduces the cost for producing polyaniline nanoparticles, and increases the yield of the polyaniline nanoparticles. Since the small amount of the surfactant is used in the present invention, the washing step for removing the micelles, which is produced with the surfactant, from the produced polyaniline nanoparticles can be greatly simplified. Namely, the amount of the solvent for the washing step and the process time for the washing step can be minimized. In addition, the polyaniline nanoparticles produced according to the present invention has the high conductivity of 200 to 300 S/cm, and is useful as an electro-magnetic material, such as an anti-static agent, an electromagnetic shielding, a magnetic recording medium, a gas sensor, an electron transport layer of a light emitting device, and so on, and is particularly suitable as a nano-cable, an alternative material of carbon fiber, and so on due to its rod shape.

Claims

[1] A method for preparing polyaniline nanoparticles, comprising the steps of:
adding a surfactant into a mixed solvent including water and an organic solvent, and stirring the surfactant to form a micelle;
adding aniline monomer into a reaction solution containing the micelle, and polymerizing the aniline monomer with a dopant and an oxidizing agent to form polyaniline; and
adding excess organic solvent to the reaction solution to separate the polyaniline and the micelle.

[2] The method for preparing polyaniline nanoparticles according to claim 1, wherein the micelle formation step is carried out at the temperature of -30 to 0 ° C.

[3] The method for preparing polyaniline nanoparticles according to claim 1, wherein the organic solvent in the mixed solvent is selected from the group consisting of methanol, ethanol, butanol, octanol, decanol and the mixtures thereof.

[4] The method for preparing polyaniline nanoparticles according to claim 1, wherein the amount of the organic solvent in the mixed solvent is 20 to 40 weight%.

[5] The method for preparing polyaniline nanoparticles according to claim 1, wherein the surfactant is selected from the group consisting of octyltrimethylammonium bromide, decyltrimethylammonium bromide, dodecyltrimethylammonium bromide, sodium dodecylsulfate, sodium dioctylsulfosuccinate and the mixtures thereof.

[6] The method for preparing polyaniline nanoparticles according to claim 1, wherein the dopant is selected from the group consisting of hydrochloric acid, sulfuric acid, phosphoric acid and the mixtures thereof.

[7] The method for preparing polyaniline nanoparticles according to claim 1, wherein the oxidizing agent is selected from the group consisting of ammonium persulfate, potassium peroxodisulfate and the mixtures thereof.

[8] The method for preparing polyaniline nanoparticles according to claim 1, wherein the surfactant is sodium dodecylsulfate, and the dopant is sulfuric acid.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C08J 3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC7 C08J 3/00, C08G 73/02, C25D 13/00, G03F 9/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Patents and applications for inventions since 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)
KIPASS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 2003-0021278 A (POSCO) 15 Mar. 2003 see the whole document	1 - 8
A	US 5240797 A (Seiko Epson Corporation) 31 Aug. 1993 see the whole document	1 - 8
A	US 5242558 A (Seiko Epson Corporation) 7 Sep. 1993 see the whole document	1 - 8

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:
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INTERNATIONAL SEARCH REPORT
Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR2003-0021278A	15.03.2003	None	
US5240797A	31.08.1993	None	
US5242558A	07.09.1993	None	